COMPLETE SPECIFICATION.

Improvements in and relating to a Process and Apparatus for the Production of Highly-Pure Silicon.

We, THE PLESSEY COMPANY LIMITED, a British Company, of Vicarage Lane, Ilford, in the County of Essex, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to processes for the manufacture of silicon.

Silicon for use in such semi-conductor devices as rectifiers and transistors has to be prepared to exceptional standards, in that it must have an impurity content which is exceedingly low by ordinary standards. The preparation of silicon to such standards is a problem of considerable technical difficulty, and the present invention is related to the provision of a process by which highly pure silicon can be obtained, and from which semi-conductor material of appropriate electrical properties can be obtained.

Silicon as generally used in semi-conductor devices includes an additive whose purpose is to produce the desired type and degree of conductivity in the semi-conductor, and which is present in minute but precisely controlled quantities. An additive element, the word element being used in its chemical sense, is an element whose valency differs from the valency of the semi-conductor element (in the present case silicon) to which it is to be added, so that when an atom thereof is incorporated into the crystal lattice of the body of the semi-conductor element, it forms a current carrier the polarity of which depends on whether the valency of the additive element is greater or less than that of the semi-conductor element. Thus if the additive element has a valency of 3, the current carriers which it produces in silicon are of positive polarity, i.e. they are holes, while if it has a valency of 5, the carriers are of negative polarity, i.e. they are electrons. An example of an additive element for silicon is, in the first case boron, and in the second case phosphorus.

The semi-conductor material of desired conductivity can be obtained by first preparing the pure silicon to a degree of purity greater than that of the final material, and then incorporating the additive(s). The invention can be used to produce silicon of a degree of purity appropriate for this use. The invention can also be used in connection with the production of a semi-conductor element, in this case silicon, with appropriate additives, directly and without first preparing the pure silicon, as described in our co-pending British Application No. 33758/56 (Serial No. 878,765).

The present invention provides a method for the preparation of highly pure silicon by the thermal decomposition of monosilane in a decomposition chamber containing a body of highly pure silicon, which comprises heating said silicon body by thermal radiation so as to reduce its electrical resistivity, and thereafter heating said silicon body by induction heating in the presence of monosilane supplied to said decomposition chamber, said heating by thermal radiation being terminated when the resistivity of said silicon body has been reduced to

a value such that said heating by induction heating can maintain said silicon body above the decomposition temperature of monosilane, whereby silicon due to the decomposition of said monosilane is deposited on said silicon body in a highly pure condition.

The present invention also provides apparatus for the preparation of silicon by the thermal decomposition of monosilane, which comprises a seed crystal of highly pure silicon supported in a decomposition chamber, a source of heat located outside said decomposition chamber from which said seed crystal can be initially heated by thermal radiation, to raise its temperature so as to reduce its electrical resistivity enough for it to be maintained by induction heating above the decomposition temperature of monosilane, an induction heating source also located outside said decomposition chamber by which said seed crystal can be subjected to heat, the heating by thermal radiation being terminated when said silicon's resistivity has been reduced enough for the induction heating source to maintain it above said decomposition temperature whereafter said seed crystal is maintained above said decomposition temperature by heat due to said induction heating source, and an input to said decomposition chamber for the supply of monosilane thereto in a highly pure condition and unadmixed with any other gas, said monosilane being directed by said input onto a surface of said seed crystal which is maintained in a molten condition by heat due to said induction heating source, whereby silicon due to the decomposition of monosilane is deposited in a highly pure crystalline form on said seed crystal.

The invention will now be described with reference to the drawings accompanying the Provisional Specification in which:—

Figure 1 is a diagrammatic view of the apparatus suited to one method of preparing pure monosilane;

Figure 2 is a diagrammatic view of apparatus according to the invention; and

Figure 3 is a section of silicon rod produced by the apparatus and process of the invention.

One method of producing pure monosilane (SiH₄) will now be described with reference to Figure 1. Other methods of producing pure monosilane are known but we have found it convenient to use the action of ammonium bromide in liquid ammonia upon magnesium silicide.

Magnesium silicide is prepared by heating an intimate mixture of magnesium and commercial grade silicon powder, preferably in the atomic ratio of 2 Mg.1Si, in an atmosphere of hydrogen. The magnesium silicide so prepared is reacted with a solution of ammonium bromide in liquid ammonia, when a high yield (up to 75%) of the monosilane SiH_4 is produced. Only a very small percentage of the higher hydrides of silicon Si_2H_6, Si_3H_8, etc., are present in the gas produced, and these may be rejected without greatly affecting the final yield of silicon. The monosilane produced by the above reaction must be further purified before it can be used for obtaining pure silicon according to the invention.

The reaction between magnesium silicide and ammonium bromide may be carried out in that part of the apparatus shown to the left of the vertical broken line in Figure 1, whilst purification is carried out in the apparatus shown to the right of this line. The reaction apparatus is made of borosilicate glass and the purification apparatus of quartz. The solution of ammonium bromide in liquid ammonia is placed in the round bottomed flask 1 which is surrounded by a low temperature bath 2 maintained at about – 50° C. The magnesium silicide is contained in two side tubes 3 which are secured in necks on the round bottomed flask 1 by means of ground glass joints. By rotating the side tubes 3 the powdered magnesium silicide can be tipped into the solution of ammonium bromide as required. Connected to the flask 1 is a valve controlled inlet 4 for the liquid ammonia and a dephlegmator 5 for refluxing most of the ammonia vaporised by the reaction. The ammonia is condensed in the tubes 6 which are surrounded by a mixture 7 of solid carbon dioxide and acetone refrigerant.

The condenser tubes 6 are connected to a heat exchanging unit 8 which serves to remove most or all residual ammonia from the gas. The heat exchanger 8 contains a coil 9 through which a refrigerant consisting of gaseous nitrogen cooled by liquid nitrogen is passed. On coming into contact with the coil 9 the gas stream is cooled to about – 100° C. and most or all residual ammonia removed. The outlet tube 10 of the heat exchanger is connected by means of borosilicate glass to quartz joint 11 to the boiler tube 12 of the purification apparatus. The boiler tube 12, which is surrounded by a suitable low-temperature bath 13 (about – 130° C.) is connected to a vacuum jacketed fractionating column 14. The fractionating column 14 is packed with small quartz spirals and terminates in a condenser 15 cooled by liquid nitrogen. Heat leakages into the column 14 from the atmosphere are offset by passing the cold nitrogen gas evaporating from the condenser 15 down between the packed column 14 and the vacuum jacket 16. A tube 17 for leading the gas from the fractionating column 14 is connected to a flow gauge 18 and to quartz filters 19 and 20. The quartz filter 19 comprises a U-tube containing quartz wool im-

mersed in a low temperature bath at about
- 78° C. The quartz filter 20 comprises a
quartz filter disc. The outlet 21 from the
purification apparatus leads to the appara-
tus for the production of pure silicon.

Various flow control taps such as 22, are
provided where required and also mano-
meters such as 23 are connected to those
points on the apparatus where a check on
the pressure is required. By means of a
tube 24 a diffusion pump can be connected
to the apparatus to enable the whole to be
evacuated.

Before the reaction between the solution
of ammonium bromide in ammonia and
magnesium silicide is commenced, the whole
apparatus is evacuated in order to prevent
oxidation of the monosilane produced; such
oxidation takes place spontaneously in air
and with some considerable violence at
ordinary temperatures and pressures. When
the apparatus has been evacuated the tubes
3 are tilted to tip some of the magnesium
silicide into the solution of ammonium
bromide whereupon a gas containing mono-
silane, ammonia, hydrogen and small
amounts of other hydrides is evolved. Most
of the ammonia is refluxed by the dephleg-
mator 5 above the reaction vessel 1 and
most of the residual ammonia removed by
the heat exchanger 8.

The monosilane flowing in the tube 10 is
then condensed in the boiler 12 of the purifi-
cation apparatus. For this the boiler tube
is surrounded by a bath containing liquid
nitrogen of boiling point - 196° C.; to start
the distillation this bath is replaced by an-
other kept at a temperature of about
- 120° C. The hydrogen present is pumped
away by means of the tube 24 connected
to the diffusion pump through a tubular
furnace, to decompose any non-condensed
monosilane in the hydrogen stream. The
liquid monosilane in the boiler 12 is caused
to evaporate by the heat from the low tem-
perature bath 13 and condenses in the con-
denser 15 at the top of the fractionating
column 14.

The liquid monosilane condensed in the
condenser 15 refluxes back onto the packing
in the fractionating column 14 and gradually
cools and wets the latter until the whole
packing is thoroughly wetted and liquid
monosilane is refluxing into the boiler 12.
After allowing a suitable time for a steady
state to be reached, the distillate is removed
from the top of the fractionating column 14
by means of the tube 17, the pure mono-
silane then being led through the flow gauge
18 and the quartz filters 19 and 20 to the
outlet 21 and thence to the decomposition
cell for the production of pure silicon.

Referring to Figure 2, the apparatus
shown is designed for carrying out the
thermal decomposition of monosilane into
its constituents, silicon and hydrogen, at
temperatures above 450° C. This thermal
decomposition may take place either at a
hot surface or in the gas phase and both
reactions can occur simultaneously. Con-
ditions are preferably chosen in the appara-
tus to be described such that the surface de-
composition of silane is favoured. Appara-
tus which is better suited to the decomposi-
tion of silane in the gas phase is described
in our co-pending British Application No.
33757/56 (Serial No. 878,764).

In the apparatus of Figure 2, a supply of
monosilane 31, purified either by the frac-
tional distillation method described or by
a gas chromatographic method, or any other
suitable method of purification, is led via
a control tap 32 and a manometer 33 to a
quartz decomposition chamber 35. The
monosilane enters the chamber 35 through
a suitably designed quartz jet tube 34 and
impinges onto a globule 36 of liquid silicon
which is held stable at the top of a high
purity silicon seed crystal 37 having a re-
sistivity of at least 50 ohm-cm. In opera-
tion during the formation of pure silicon the
globule of silicon 36 is maintained in liquid
form by means of a water cooled copper
inductor loop 40 placed outside the cham-
ber 5. This inductor loop 40 is supplied
with high frequency alternating current from
a suitably designed high power generator
(not shown), the operating frequency being
suitably between 300 kc/s and 1 mc/s.

The resistivity of the high purity silicon
seed 37 is too high at room temperature for
the initial heating of the seed by the high
frequency inductor loop 40. Therefore, an
initial temperature rise is created in the seed
37 in order to lower the resistivity and this
may be brought about by focusing a heat
source for example a high wattage electric
lamp on the seed 37 by means of an ellip-
soidal mirror or a pair of parabolic mirrors.
Alternatively in order to effect the required
initial temperature rise an electrically con-
ductive annulus of any suitable high melting
point metal, such as molybdenum or tung-
sten or high purity de-gassed graphite may
be placed concentrically around the seed 37
and is heated by induction heating for ex-
ample by coupling with the inductor loop
40 and thus heats the seed by direct radia-
tion to the required temperature, usually
between 500 and 1,000° C. When this tem-
perature has been reached the annulus is
quickly removed so that direct coupling may
then exist between the seed 37 and the
inductor loop 40, and the seed remaining
hot by absorbing the high frequency power
from the loop. This latter method however
suffers from the disadvantage that materials
are introduced into the chamber 5 which
give off a vapour that may lead to an im-
purity being formed in the silicon. For

this reason the elliptical mirror method, wherein the heating arrangements for the seed 37 are all located outside the decomposition chamber, is preferred, as this avoids introducing foreign materials into the decomposition chamber.

Once preheating has been established, the high frequency power dissipation in the silicon seed 37 is greatly increased and the top of the seed forms into the molten globule 36. The design of the inductor loop 40 and position of the silicon seed 37 in the field of the loop are so arranged that it is possible to hold the liquid blob 36 stably on the top of the seed crystal. The shape of the liquid-solid interface 44 produced between the liquid blob 36 and the crystal 37 is in practice convex towards the liquid, which condition facilitates single crystal growth.

As during the process some silicon is deposited on the inner walls of the chamber 35, the chamber is provided with an extension window 45 which does not become so coated and which always provides a means of sighting the seed 37 and the liquid globule 36.

The position of the crystal seed 37 can be varied relative to the inductor loop 40 by means of the centreless ground quartz rod 39 to which the crystal seed 37 is secured by means of a quartz support 38. The quartz rod 39 is so mounted in a base 43 provided for the apparatus, that it can be rotated during the deposition of silicon, a seal being provided between the quartz rod 39 and the base 43 by means of a high vacuum rubber seal 50. Connection between the chamber 35 and the base 43 is provided by means of a water cooled metal cone 41 which engages a ground socket 51 on the chamber. The outlet 42 from the base 43 leads through a further metal-ground quartz joint 52 to a high vacuum pump (not shown) for evacuating the apparatus.

Once the desired operating conditions for the apparatus have been attained the monosilane emerging from the jet tube 34 decomposes at the liquid silicon surface and the silicon so formed enters the liquid globule whilst the hydrogen is drawn off through the outlet 42 by means of the vacuum pump. As the deposited silicon enters the globule 36, the seed 37 is slowly rotated and withdrawn from the chamber at a rate equivalent to that at which silicon is deposited from the vapour phase so that the liquid-solid interface remains approximately stationary relative to the inductor loop 40. In this manner a continuous rod of densified silicon is built up on the seed crystal. If the seed crystal 37 is monocrystalline then single crystal silicon is obtained from the material that solidifies from the liquid, whilst the use of a polycrystalline seed results in polycrystalline silicon but the orientation of the seed

crystal grains is carried on throughout the material deposited in the liquid.

An extraneous polycrystalline over-growth is obtained as some monosilane decomposes on those parts of the seed 37 below the liquid-solid interface where the temperature is greater than 450° C. This extraneous over-growth also takes place at the liquid-solid interface, since any monosilane present there may decompose either on the liquid or the solid surface. However, this extraneous over-growth does not cause stray nucleation towards the centre of the seed because of the convexity of the liquid-solid interface towards the liquid which causes this over-growth to extend outwards from the seed 37.

The type of silicon build up obtained by the method and apparatus of this invention can be seen from Figure 3. In this figure an original seed crystal 56, in this case a single crystal, is shown together with a build up of deposited silicon material 57 which is also monocrystalline and of the same orientation as the seed crystal 56. An extraneous polycrystalline over-growth is indicated at 58 as a thin crust around the silicon rod. The dotted line 59 shows the top of the original crystal seed 56.

In order to favour the decomposition of monosilane at the surface of the liquid globule 36 the decomposition is carried out at a reduced pressure. The control valve 32 is adjusted so that the monosilane pressure on the inlet side of the jet 34 is 0.5 to 1.0 cms. of mercury, the chamber being continuously evacuated by means of the vacuum pump connected to the aperture 42 so that this jet pressure is maintained. Under these conditions a mass of from 1.5 to 5 grams of silicon per hour is deposited on the seed 37, the exact amount deposited depending on the exact value of the jet inlet pressure. It is found that the lower the jet inlet pressure the greater the proportion of surface decomposition to gas phase decomposition. Silicon produced in the gas phase decomposition is swept to the walls of the chamber 35 as an amorphous brown deposit which eventually obscures vision through the main part of the chamber.

Generally speaking we have found that the higher the jet inlet pressure the lower the proportion of surface decomposition to gas phase decomposition and the greater the deposition rate because the input rate of monosilane has increased. These observations apply essentially to low pressure conditions and experiments carried out on the decomposition of silane at 40 to 60 cms. Hg pressure when the proportion of surface decomposition to gas phase decomposition is very low, indicate that the rate of deposition on the seed 37 is negligible. The surface decomposition of monosilane is preferred but in order to attain a suitable production rate

a compromise is made between those conditions which favour a gas phase decomposition and those which favour a surface decomposition and in practice silicon is deposited on the seed 37 at the rate of about 5 grams per hour, which corresponds roughly to a 1 : 1 ratio between surface and gas phase decomposition.

It should be emphasised that the deposition rates and reaction proportions mentioned above are dependent on the physical arrangement of the jet system in relation to the inductor loop, the position of the seed crystal and the design of the chamber.

From the preceding description it will have been noted that, unlike certain known processes in which silicon is produced by the thermal decomposition of monosilane, no carrier gas is used to convey the monosilane into the decomposition zone. This simplifies the process in that the need, present in such known processes, of producing the aforementioned carrier gas in a state of purity comparable with that of the monosilane, is avoided. Furthermore, any risk that the silicon can be contaminated by the carrier gas itself is also eliminated.

WHAT WE CLAIM IS:—

1. A method for the preparation of a highly pure silicon by the thermal decomposition of monosilane in a decomposition chamber containing a body of highly pure silicon, which comprises heating said silicon body by thermal radiation so as to reduce its electrical resistivity, and thereafter heating said silicon body by induction heating in the presence of monosilane supplied to said decomposition chamber, said heating by thermal radiation being terminated when the resistivity of said silicon body has been reduced to a value such that said heating by induction heating can maintain said silicon body above the decomposition temperature of monosilane, whereby silicon due to the decomposition of said monosilane is deposited on said silicon body in a highly pure condition.

2. A method as claimed in Claim 1, and in which said monosilane is supplied to said decomposition chamber unadmixed with any other gas.

3. A method as claimed in Claim 2, and in which said monosilane is supplied to the decomposition chamber via a jet which is directed on to a surface of said silicon body which, after the termination of heating by thermal radiation, is maintained in a molten condition by said induction heating.

4. A method as claimed in Claim 2 or 3, and in which the conditions of temperature and pressure in the decomposition chamber when the monosilane is undergoing thermal decomposition are such that the decomposition occurs partly as a gas phase reaction and partly as a reaction occurring at the surface of said silicon body.

5. A method as claimed in Claim 2, 3 or 4, in which the source of heat for effecting said heating by thermal radiation is located outside the decomposition chamber, and in which the source of heat for effecting said heating by induction heating is also located outside the decomposition chamber, whereby the sources of said heating are located wholly without said decomposition chamber.

6. A method as claimed in Claim 5, and in which said source of heat for said thermal radiation heating includes a heat source and a mirror or mirrors adapted to direct heat from said source on to said silicon body.

7. A method as claimed in Claim 6, and in which said source of heat for thermal radiation heating is an electric lamp.

8. A method as claimed in Claim 2, 3 or 4, and in which the source of heat for effecting said heating by thermal radiation consists of an electrically conductive annulus which is placed in said decomposition chamber adjacent to and embracing said body of silicon, said electrically conductive annulus being heated by induction heating.

9. A method as claimed in Claim 8, in which said electrically conductive annulus is heated by induction heating from the same source of heat which heats the silicon body by induction heating, and in which said termination of thermal radiation heating is effected by removing said annulus from the vicinity of said silicon body.

10. A method for producing silicon, substantially as described with reference to the drawings accompanying the Provisional Specification.

11. Apparatus for the preparation of silicon by the thermal decomposition of monosilane, which comprises a seed crystal of highly pure silicon supported in a decomposition chamber, a source of heat located outside said decomposition chamber from which said seed crystal can be initially heated by thermal radiation to raise its temperature so as to reduce its electrical resistivity enough for it to be maintained by induction heating above the decomposition temperature of monosilane, an induction heating source also located outside said decomposition chamber by which said seed crystal can be subjected to heat, the heating by thermal radiation being terminated when said silicon's resistivity has been reduced enough for the induction heating source to maintain it above said decomposition temperature, whereafter said seed crystal is maintained above said decomposition temperature by heat due to said induction heating source, and an input to said decomposition chamber for the supply of monosilane thereto in a highly pure condition and unadmixed with

any other gas, said monosilane being directed by said input on to a surface of said seed crystal which is maintained in a molten condition by heat due to said induction heating source, whereby silicon due to the decomposition of monosilane is deposited in a highly pure crystalline form on said seed crystal.

12. An apparatus in accordance with Claim 11, and in which said source of heat for heating by thermal radiation comprises an electric lamp, and a mirror or mirrors associated therewith for directing heat from said lamp on to said silicon seed crystal.

13. An apparatus for the production of highly pure silicon substantially as described with reference to the drawings accompanying the Provisional Specification.

14. Silicon when produced by a method as claimed in any one of Claims 1 to 10, or by apparatus as claimed in Claim 11, 12 or 13.

A. A. THORNTON & CO.,
Chartered Patent Agents,
Northumberland House,
303—306 High Holborn,
London, W.C.1,
For the Applicants.

Reference has been directed, in pursuance of Section 8 of the Patents Act, 1949, to Specification No. 826,575.

PROVISIONAL SPECIFICATION.

Improvements in and relating to a Process and Apparatus for the Production of Highly-Pure Silicon.

We, THE PLESSEY COMPANY LIMITED, a British Company, of Vicarage Lane, Ilford, Essex, do hereby declare this invention to be described in the following statement:—

This invention relates to processes for the manufacture of semi-conductor materials.

Semi-conductor materials for use in rectifiers, transistors and the like are required to be prepared to exceptional standards, in that the material must have an impurity content which is exceedingly small by ordinary standards, and must contain an additive necessary for producing the desired type and degree of conductivity, in an amount which is also exceedingly small. The content of the additive must nevertheless be precisely controlled.

In the past, the preparation of semi-conductor material to these requirements has been a problem of considerable technical difficulty, and the present invention is concerned with improvements by which a semi-conductor material of desired chemical composition can be obtained, and from or by which material of appropriate electrical properties can be obtained.

Once the semi-conductor of the necessary high degree of purity is obtained there can be added to it the additive material which is required to produce the desired type and degree of conductivity. This obviously requires that the semi-conductor, before the addition of the additive material, must have a substantially greater purity than the final material. The present invention lends itself to the production of a material of this degree of purity.

The invention can also be used in connection with the production of a semi-conductor material, with appropriate additives, directly and without first preparing the pure semi-conductor material, as described in our co-pending Application No.   of even date.

The invention is particularly, but not exclusively applicable to the manufacture of silicon. In a preferred embodiment of the invention described hereinafter, silicon is prepared from silane.

Where initially "pure" semi-conductor is used there is a substantial difficulty not only in producing it in the required high degree of purity, but also in determining the actual purity of the material. For example, spectrographic techniques are not satisfactory and recourse must usually be had to other methods of analysis.

One test for the purity of silicon is its resistivity. It has been calculated that ultimately pure monocrystalline silicon has a high resistivity of the order of 2×10^5 ohms-cm., but the resistivity is lowered if impurities are present. Also, this figure can be achieved and even exceeded if donor and acceptor impurities are present in exactly equal numbers. Resistivity alone is thus not a test of purity unless it can be established by, say, Hall effect measurement that substantially only one type of impurity is present.

In carrying the present invention into effect the semi-conductor material is prepared by a decomposition of a gaseous compound of the semi-conductor to cause the deposition of the semi-conductor on the surface of a body of the semi-conductor.

In a preferred apparatus for carrying out the invention a seed crystal of substantially pure semi-conductor is mounted within a vacuum chamber having external heating means for melting a portion of said crystal, means being provided in said chamber for

directing a stream of pure gaseous compound onto the melted portion of the crystal so as to bring about the decomposition of said compound and the growth on said seed crystal of a crystal of the semi-conductor.

In particular, the invention can be applied to the production of silicon from one of the silanes.

In order that the invention may be well understood it will now be described in detail with reference to the accompanying drawings, in which:—

Figure 1 is a diagrammatic view of apparatus suited to one method of preparing pure silane;

Figure 2 is a diagrammatic view of apparatus according to the invention; and

Figure 3 is a section of silicon rod produced by the apparatus and process of the invention.

One method of producing pure silane will now be described with reference to Figure 1 of the accompanying drawings. Other methods of producing pure silane are known but we have found it convenient to use the action of ammonium bromide in liquid ammonia upon magnesium silicide.

Magnesium silicide is prepared by heating an intimate mixture of magnesium and commercial grade silicon powder, preferably in the atomic ratio of 2 Mg: Si, in an atmosphere of hydrogen. The magnesium silicide so prepared is reacted with a solution of ammonium bromide in liquid ammonia when a high yield (up to 75%) of the monosilane SiH_4 is produced. Only a very small percentage of the higher hydrides of silicon Si_2H_6, Si_3H_8, etc., are present in the gas produced and these may be rejected without greatly affecting the final yield of silicon. The monosilane or silane produced by the above reaction must be further purified before it can be used for obtaining pure silicon according to the invention.

The reaction between magnesium silicide and ammonium bromide may be carried out in that part of the apparatus shown to the left of the vertical broken line in Figure 1, whilst purification is carried out in the apparatus shown to the right of this line. The reaction apparatus is made of pyrex glass and the purification apparatus of quartz. The solution of ammonium bromide in liquid ammonia is placed in the round bottomed flask 1 which is surrounded by a low temperature bath 2 maintained at about −50° C. The magnesium silicide is contained in two side tubes 3 which are secured in necks on the round bottomed flask 1 by means of ground glass joints. By rotating the side tubes 3 the powdered magnesium silicide can be tipped into the solution of ammonium bromide as required. Connected to the flask 1 is a valve controlled inlet 4 for the liquid ammonia and a

dephlegmator 5 for refluxing most of the ammonia vaporised by the reaction. The ammonia is condensed in the tubes 6 which are surrounded by a mixture 7 of solid carbon dioxide and acetone refrigerant. The condenser tubes 6 are connected to a heat exchanging unit 8 which serves to remove most or all residual ammonia from the gas. The heat exchanger 8 contains a coil 9 through which a refrigerant consisting of gaseous nitrogen cooled by liquid nitrogen is passed. On coming into contact with the coil 9 the gas stream is cooled to about −100° C. and most or all residual ammonia removed. The outlet tube 10 of the heat exchanger is connected by means of a pyrex to quartz joint 11 to the boiler tube 12 of the purification apparatus. The boiler tube 12, which is surrounded by a suitable low-temperature bath 13 (about −130° C.) is connected to a vacuum jacketed fractionating column 14. The fractionating column 14 is packed with small quartz spirals and terminates in a condenser 15 cooled by liquid nitrogen. Heat leakages into the column 14 from the atmosphere are offset by passing the cold nitrogen gas evaporating from the condenser 15 down between the back column 14 and the vacuum jacket 16. A tube 17 for leading the gas from the fractionating column 14 is connected to a flow gauge 18 and to quartz filters 19 and 20. The quartz filter 19 comprises a U-tube containing quartz wool immersed in a low temperature bath in about −78°. The quartz filter 20 comprises a quartz filter disc. The outlet 21 from the purification apparatus leads to the apparatus for the production of pure silicon.

Various flow control taps such as 22, are provided where required and also manometers such as 23 are connected to those points on the apparatus where a check on the pressure is required. By means of a tube 24 a diffusion pump can be connected to the apparatus to enable the whole to be evacuated.

Before the reaction between the solution of ammonium bromide in ammonia and magnesium silicide is commenced, the whole apparatus is evacuated in order to prevent oxidation of the silane produced which oxidation takes place spontaneously in air and with some considerable violence at ordinary temperatures and pressures. When the apparatus has been evacuated the tubes 3 are tilted to tip some of the magnesium silicide into the solution of ammonium bromide whereupon a gas containing monosilane (or silane), ammonia, hydrogen and small amounts of other hydrides is evolved. Most of the ammonia is refluxed by a dephlegmator 5 above the reaction vessel 1 and most of the residual ammonia removed by the heat exchanger 8. The crude silane flowing in the tube 10 is then condensed in 130

the boiler 12 of the purification apparatus. For this the boiler tube is surrounded by a bath containing liquid nitrogen BP – 196° C. To start the distillation this bath is replaced by another kept at a temperature of about – 120° C. The hydrogen present is pumped away by means of the tube 24 connected to the diffusion pump, through a tubular furnace, to decompose any non-condensed silane in the hydrogen stream. The liquid silane in the boiler 12 is caused to evaporate by the heat from the low temperature bath 13 and condenses in the condenser 15 at the top of the fractionating column 14. The liquid silane condensed in the condenser 15 refluxes back onto the packing in the fractionating column 14 and gradually cools and wets the latter until the whole packing is thoroughly wetted and liquid silane is refluxing into the boiler 12. After allowing a suitable time for a steady state to be reached, the distillate is removed from the top of the fractionating column 14 by means of the tube 17 the pure silane then being led through the flow gauge 18 and the quartz filters 19 and 20 to the outlet 21 and thence to the decomposition cell for the production of pure silicon.

Referring to Figure 2, the apparatus shown is designed for carrying out the thermal decomposition of monosilane (or silane) into its constituents, silicon and hydrogen, at temperatures above about 450° C. This thermal decomposition may take place either at a hot surface or in the gas phase and both reactions can occur simultaneously. Conditions are chosen in the apparatus to be described such that the surface decomposition of silane is favoured. Apparatus which is better suited to the decomposition of silane in the gas phase forms the subject matter of our copending Application No.   of equal date.

In the apparatus of Figure 2, a supply of silane 1, purified either by the fractional distillation method described or by a gas chromatographic method, or any other suitable method of purification, is led via a control tap 2 and a manometer 3 to a quartz decomposition chamber 5. The silane enters the chamber 5 through a suitably designed quartz jet tube 4 and impinges onto a blob of liquid silicon 6 which is held stable at the top of a high purity silicon seed crystal 7 having a resistivity of at least 50 ohm-cm. In operation during the formation of pure silicon the blob of silicon 6 is maintained in liquid form by means of a water cooled copper inductor loop 10 placed outside the chamber 5. This inductor loop 10 is supplied with high frequency alternating current from a suitably designed high power valve generator (not shown) the operating frequency is suitably between about 300 kC/s. to 1 Mc/s. However, the resistivity of the high purity silicon seed 7 is too high at room temperature for the initial heating of the seed by the high frequency inductor loop 10. Therefore, an initial temperature rise must be created in the seed 7 in order to lower the resistivity and this may be brought about by focusing a high wattage electric lamp on the seed 7 by means of an ellipsoidal mirror or pair of parabolic mirrors. Alternatively, in order to effect the required initial temperature rise an annulus of any suitable high melting point metal, such as molybdenum tungsten etc. or high purity degassed graphite may be placed concentrically around the seed 7 such that it couples well with the inductor loop 10 and thus heats the seed by direct radiation to the required temperature, usually between 500 and 1,000° C. When this temperature has been reached the annulus is quickly removed so that direct coupling may then exist between the seed 7 and the inductor loop 10, the seed remaining hot by absorbing the high frequency power from the loop. This latter method however suffers from the disadvantage that materials are introduced into the chamber 5 which give off a vapour that may lead to an impurity being formed in the silicon.

Once preheating has been established, preferably by the elliptical mirror method as this avoids introducing foreign materials into the decomposition chamber, the high frequency power dissipation in the silicon seed 7 is greatly increased and the top of the seed forms into the molten blob 6. The design of the inductor loop 10 and position of the silicon seed 7 in the field of the loop are so arranged that it is possible to hold the liquid blob 6 stably on the top of the seed crystal. The shape of the liquid-solid interface produced between the liquid blob 6 and the crystal 7 is convex towards the liquid, which condition facilitates single crystal growth.

As during the process some silicon is deposited on the inner walls of the chamber 5, the chamber is provided with an extension window 15 which does not become so coated and which always provides a means of sighting the seed 7 and the liquid blob 6.

The position of the crystal seed 7 can be varied relative to the inductor loop 10 by means of the centreless ground quartz rod 9 to which the crystal seed 7 is secured by means of a quartz support 8. The quartz rod 9 is so mounted in a base 23 provided for the apparatus, that it can be rotated during the deposition of silicon, a seal being provided between the quartz rod 9 and the base 23 by means of a high vacuum rubber seal 20. Connection between the chamber 5 and the base 23 is provided by means of water cooled metal cones 11 and ground quartz sockets 21 on the chamber. The base 23 is connected through an aperture 12

and by a further metal-ground quartz joint 22 to a high vacuum pump for evacuating the apparatus.

Once the desired operating conditions for the apparatus have been attained the silane emerging from the jet tube 4 decomposes at the liquid silicon surface and the silicon so formed enters the liquid blob, whilst the hydrogen is drawn off through the aperture 12 by means of the vacuum pump. As the deposited silicon enters the liquid blob 6, the seed 7 is slowly rotated and withdrawn from the chamber at a rate, equivalent to that at which silicon is entering the liquid from the vapour phase so that the liquid-solid interface remains stationary relative to the inductor loop 10. In this manner a continuous rod of densified silicon is built up on the seed crystal. If the seed crystal 7 is mono-crystalline then single crystal silicon is obtained from the material that solidifies from the liquid, whilst the use of a poly-crystalline seed results in polycrystalline silicon but the orientation of the seed crystal grains is carried on throughout the material deposited in the liquid.

An extraneous polycrystalline over-growth is obtained as some silane decomposes on those parts of the seed 7 below the liquid-solid interface where the temperature is greater than 450° C. This extraneous over-growth also takes place at the liquid-solid interface, since any silane present there may decompose either on the liquid or the solid surface. However, this extraneous over-growth does not cause stray nucleation towards the centre of the seed because of the convexity of the liquid-solid interface towards the liquid which causes this over-growth to extend outwards from the seed 7.

The type of silicon build up obtained by the method and apparatus of this invention can be seen from Figure 3. In this figure an original seed crystal 16, in this case a single crystal, is shown together with a build up of deposited silicon material 17 which is also monocrystalline and of the same orientation as the seed crystal 16. An extraneous polycrystalline over-growth is indicated at 18 as a thin crust around the silicon rod. The dotted line 19 shows the top of the original crystal seed 16.

In order to favour the decomposition of silane at the surface of the liquid blob 6 the decomposition is carried out at a reduced pressure. The control valve 2 is adjusted so that the silane pressure on the inlet side of the jet 4 is about 0.5 to 1.0 cms of Hg, the chamber being continuously evacuated by means of the vacuum pump connected to the aperture 12 so that this jet pressure is maintained. Under these conditions a mass of from 1.5 to 5 grams of silicon per hour is deposited on the seed 7, the exact amount deposited depending on the exact value of the jet inlet pressure. It is found that the lower the jet inlet pressure the greater the proportion of surface decomposition to gas phase decomposition. Silicon produced in the gas phase decomposition is swept to the walls of the chamber 5 as an amorphous brown deposit which eventually obscures vision through the main part of the chamber.

Generally speaking we have found that the higher the jet inlet pressure the lower the proportion of surface decomposition to gas phase decomposition and the greater the deposition rate because the input rate of silane has increased. These observations apply essentially to low pressure conditions and experiments carried out on the decomposition of silane at 40 to 60 cms. Hg pressure when the proportion of surface decomposition to gas phase decomposition is very low, indicate that the rate of deposition on the seed 7 is negligible. The surface decomposition of silane is preferred in this invention but in order to attain a suitable production rate a compromise is made between those conditions which favour a gas phase decomposition and those which favour a surface decomposition and in practice silicon is deposited on the seed 7 at the rate of about 5 grams per hour, which corresponds roughly to a 1:1 ratio between surface and gas phase decomposition.

Variations and modifications of the invention may be made without departing from the scope thereof. Thus it should be emphasised that the deposition rates and reaction proportions mentioned above are dependent on the geometry of the jet system in relation to the inductor loop, position of the seed crystal and the design of the chamber and that, whereas the operating conditions mentioned give the purest silicon obtainable by this process at present, it is hoped by further experiments and research to improve the design of the overall apparatus and process.
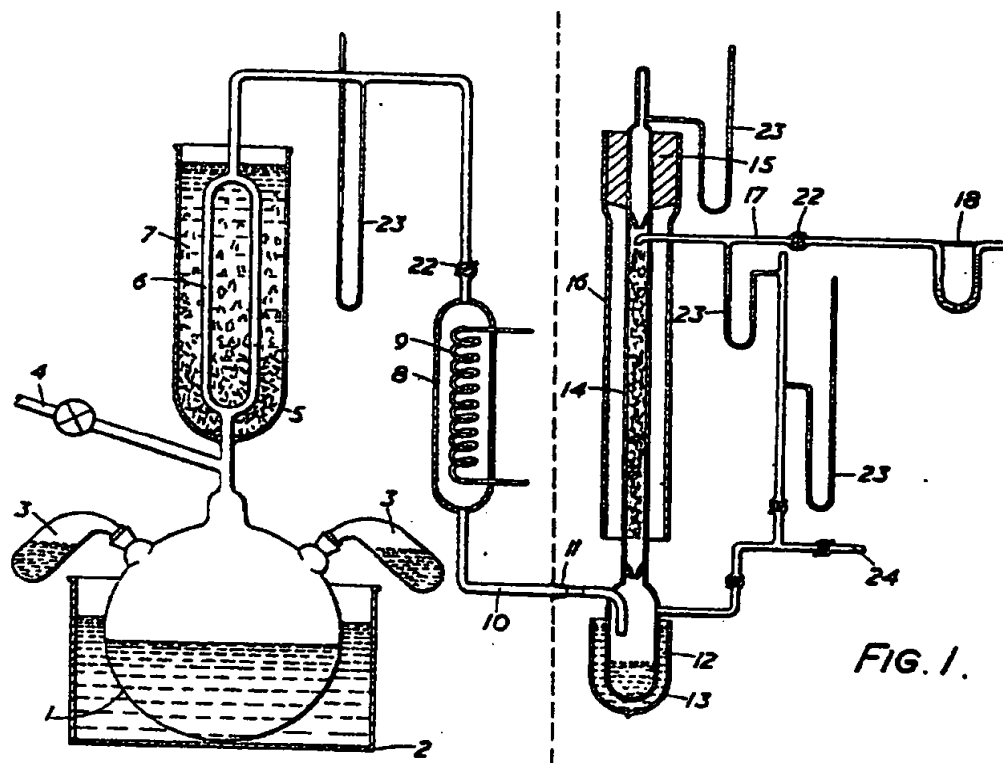
FIG. 1.

878,763   PROVISIONAL SPECIFICATION
1 SHEET   *This drawing is a reproduction of
the Original on a reduced scale.*

FIG. 1.

FIG. 2.
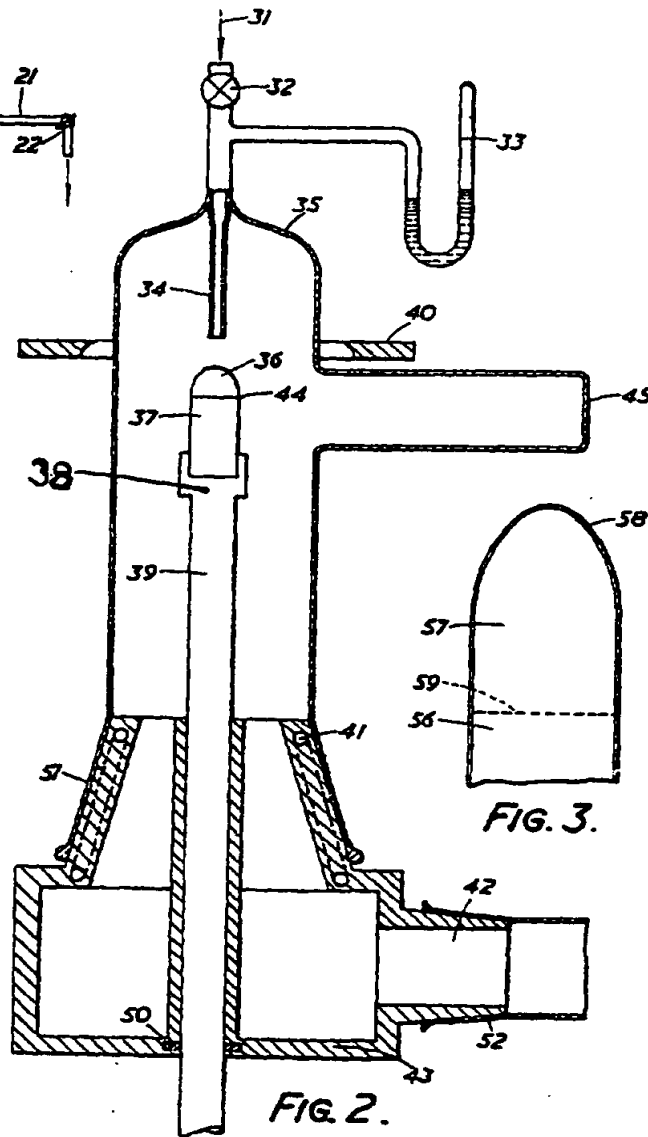
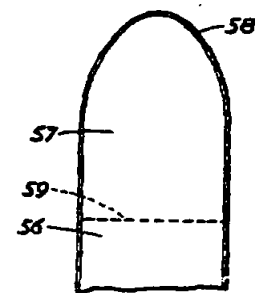FIG. 3.

FIG. I.

FIG. 2.

FIG. 3.